RESERVATIONS CONCERNING THE USE OF "MODEL COMPOUNDS" FOR COALS

John Larsen
Department of Chemistry
Lehigh University
Bethlehem, PA 18015

INTRODUCTION

A major goal in coal chemistry is understanding the chemical reactions which occur in coals, especially those reactions which occur during coal conversion. One frequently used approach is to study the reaction of compounds which are thought to contain specific functional groups which occur in coals and assume these functional groups will react identically in the coal and in the model system. This paper is an exploration of the "model compound" approach and an attempt to develop criteria for judging the relevance of "model compound" studies to more complex coal systems.

To provide correct insights into the chemistry which occurs during a reaction of a coal, three major criteria must be met: 1) The functional group being studied must exist in coals and its reactivity range in coals due to different substituent effects must be understood and explicitly considered. 2) Knowledge of the reaction environment in the coal must be understood at a level which allows reactivity to be corrected for differences in environment. This includes correcting reactions for "solvent effects". 3) The actual reaction occurring in the coal must be identified and understood. If all these criteria are met, the use of "model compounds" can be a very powerful means for exploring coal reactivity. If even one of the criteria is not met, then the "model compound" study may not provide insight into the chemistry occurring in the coal.

It is my belief that our knowledge of coal structure is sufficiently incomplete to make the routine utilization of model compounds unwise. A wise approach is to identify a reaction which is occurring in coals and then to develop a thorough understanding of that reaction and how it will be altered when it occurs in a coal's macromolecular system. This will involve work with pure compounds, some of which may be, but do not need to be, directly representative of coal structures. Often, the greatest insight into reactions comes from working at the extremes of reactivity. It is much better to understand the reaction thoroughly than it is to carry out an incompletely understood reaction on molecules which are believed to be representative of structures which occur in coals. Once the reaction is understood, attempts can be made to extrapolate this chemistry into the complex macromolecular coal system. In doing this, it is incumbent upon us to explicitly recognize the uncertainties in that extrapolation which derive from our uncertainties about the structure of coals. The work should come full circle. It will start with a study of real coals to identify an important reaction. This stage should be thorough enough to provide certainty as to the identity of that reaction. Then the laboratory or the library is used to gain a mastery of that particular reaction. With a thorough understanding of the reaction in hand, one then moves back to predictions about the

behaviors of coals by considering the effects of the coal medium and
structure on the understood reaction, completing the circle.

I will consider briefly our state of knowledge in the three areas I
regard as crucial: coal structure, coal as a reaction environment,
and our knowledge of the reactions which are actually occurring in
coals. My conclusion is that our knowledge in all three areas is
sufficiently uncertain to make extrapolations from routine
"model compound studies" to coals quite unreliable, and the circular
experimental pathway described above is strongly recommended.

Our knowledge of the functional groups which are present in coals has
increased enormously, but is still inadequate in some major areas.
Consider first our knowledge of the composition of coals. Finseth
has recently demonstrated that significant errors in the hydrogen
content can derive from incomplete drying of coals under conditions
currently in wide use for drying coals.[1] Oxygen content is usually
done by difference, a procedure which concentrates all of the errors
here. A recent paper compared many different methods for oxygen
analysis and showed that they give divergent results in a
non-systematic way.[2] There remain significant problems in the
routine determination of the composition of coals. It would be nice
to have well checked, very accurate compositional data for all of the
Argonne coals which explicitly include consideration of the
analytical difficulties.

The oxygen functional group distribution has received much attention.
Stock has done a magnificent job in determining the oxygen functional
group distribution of Illinois No. 6 coal.[3] This was a major
research undertaking, and I believe this is the only coal for which a
complete and reasonably detailed oxygen functional group distribution
has been published. Liotta has published some detailed information
on oxygen functional group distribution in a Rawhide (Wyodak
subbituminous) coal, and there are attempts to characterize oxygen
using NMR spectroscopy without chemical derivatization.[4,5] This
latter work provides no information about substitution patterns,
which are important. Stock has provided some information on the
number of aromatic rings which have two oxygen functionalities. This
seems to be all that is available. This is an important issue
because of the possibility of large substituent effects. Important
simple questions remain unanswered. What is the distribution of the
phenolic hydroxyls or ethers over the different polynuclear aromatic
systems? A 9-phenanthryl ether often reacts very differently than
does a   phenyl ether. What is the size distribution of the alkyl
chains in aralkyl ethers? To fully understand the behavior of a
functional group, the range of coal structures in which it occurs
must be known. NMR techniques to explore the environment of oxygen
atoms using cross-polarization are under development.[6]

The introduction of sophisticated NMR techniques has made possible
the determination of the range of PNA structures in coals[6] and this
has been done for all of the Argonne premium coals.[7] But, in spite
of the advances in NMR, there are still major disagreements about the
ring size distributions of the aromatics in coals.[8] Our knowledge of
aliphatic structures is not as great. In fact, only recently have
definitive structural assignments been made of a majority of the
aliphatic carbons in a single coal.[9] Only recently have there been
attempts to quantitatively explore the number of acidic carbon sites

in coals.[10] There are few, if any, functional groups whose population in several coals of varying rank is unquestioned.

Coals are horrendously complex reaction environments. As mined, they are glassy macromolecular systems containing a complex pore structure.[11] Molecular diffusion through glassy materials is very slow and many organic reactions of coals carried out at or near room temperature are mass transport limited.[4,12] Coals imbibe many solvents and swell in the process. With strongly swelling solvents such as pyridine, the glass-to-rubber transition is suppressed significantly below room temperature and the coals are in a rubbery state.[13] Diffusion rates in the rubbery state are enhanced by several orders of magnitude over those in the corresponding glass. The rubbery coal is still a macromolecular system which does not dissolve, so the kind of intimate mixing familiar in solution reactions does not occur. The reagent must gain access to the reaction site by diffusing through a rubbery solid. There will usually be significant mass transfer constraints on reactions of coals which involve reagents even if the coals are rubbery.

Even in reactions which do not involve an outside reagent but which are initiated within the coal, mass transport plays a role. If thermal bond homolysis occurs in a coal, the pair of radicals produced may be constrained to stay near each other by large cage effects. If the coal is still glassy, they will not be able to separate rapidly because of the absence of large scale molecular motion. If the coal is rubbery, cage effects will be much less, but the ultimate translational freedom of the radicals will be limited by their position in the coal macromolecular structure. They may not be able to diffuse to their most thermodynamically or kinetically favorable reaction partner, but may be forced by the constraints of the macromolecular system to react with a nearby group. To understand reactions in coals, the environment of the intermediates must be known, at least on a statistical basis. No information of this sort has been published. The very important work of Poutsma, Buchanan and co-workers has demonstrated another pathway for radical diffusion. They have recently shown that radicals can migrate across a plane of molecules bonded to a silica surface by sequential hydrogen abstraction reactions.[14] This is a crucial observation since it provides a mechanism for the rapid diffusion of a reactive center through the coal and justifies ignoring diffusional limitations for a range of radical reactions. Some mechanism of this sort must be involved in the artificial coalification experiments of Winans et al. which are catalyzed by clays, yet which occur throughout the mass of the sample, not just adjacent to the clay surface.[15] Whether the intermediates involved are radicals or ions has not been established.

One other aspect of the macromolecular nature of coal has important effects on reactivity. It is that coals are selective absorbents.[16] While extensive work has been done to model coal reactivity containing good hydrogen donors like tetralin, the composition of the reacting coal in any direct liquefaction process has never been defined. The coal will have been swollen by components from the recycle solvent. It has been documented extensively that coals are selective absorbents and that they do not have a large affinity for aliphatic materials.[16-18] The reacting coal system will consist of coal and an unknown mixture of components selectively extracted from

the recycle oil, probably in about equal amounts. Modeling coal
conversion processes using model compounds will be a fatuous activity
until the reacting system has been adequately defined. The same
constraints do not apply to pyrolysis reactions, but there cage
effects and other mass transport issues become complex and difficult
to handle.

The last issue to be discussed is the nature of the reactions which
are occurring in coals. There is general agreement that radical
reactions are involved in coal conversion. An early simplistic
mechanism that the reaction proceeded totally by bond homolysis
followed by "capping" of the radicals by hydrogen donors has largely
been replaced by the realization that a variety of chain processes
are occurring in addition to the simple homolytic bond cleavage.[19,20]
The extent and role of these chain reactions is still an object of
much discussion. The family of radical reactions which are occurring
still has not been completely elucidated. The use of probe molecules
should be a major help.[21]

Radical reactions may not be the only ones occurring. Brower has
published impressive evidence based on volumes of activation and
isotope effects that ionic and/or electrocyclic processes must be
occurring during coal liquefaction.[22] I have yet to see a convincing
explanation for or rationalization of Brower's data. Ross has
recently become concerned with ionic reactions occurring at the
coal-mineral matter interface.[23] Much chemistry is possible here as
demonstrated by the Winans' coalification experiment. Its role in
coal conversion, if any, has not yet been elucidated. Finally, there
is the whole question of radical anion and radical cation chemistry.

In summary, there is abundant evidence for the existence of a variety
of radical processes occurring during coal conversion. The snarl of
competing and parallel reactions has not yet been unraveled. There
exists evidence that the principle pathways may not be solely radical
reactions, and this evidence has been largely ignored. It seems clear
that one must deal with complex radical chemistry when considering
coal conversion and coal pyrolysis. Whether radical reactions are
the only pathways which must be considered is not yet clear.

Coal is perhaps the most complex organic material whose structure and
reactivity has been systematically studied. It is a largely
insoluble, black, amorphous, inhomogeneous system containing a wide
variety of structural groups and a respectable population of free
radicals, and it is not surprising that the progress has been slow
and difficult. I believe that achieving the most rapid progress
possible requires explicit recognition and acceptance of the enormous
complexity of the material. There have been many model compound
studies published in which many of the structural complexities are
ignored. The use of simplified models and procedures imposes the
duty to identify the simplifying assumptions and their potential
impact on any conclusions reached.

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